Swami Ramanand Teerth Marathwada University, Nanded, Maharashtra, India

(UGC Recognized, NAAC Re-accredited 'B++' grade State University)

" Study of optimization and characterization of aryl diazonium salt doped chemiresistive metal oxide gas sensors."

Research Proposal Submitted
In Fulfillment of Registration to
Ph.D. Programme

In the Subject
Physics Faculty of Science & Technology

Submitted by
Mr.Sandip Anjiram Jadhav
Research Student
Shri. Shivaji College
Parbhani, 431401

Under the Supervision of
Dr. S.M. Yenorkar
Professor
Shri. Shivaji College
Parbhani - 431401

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Department of Physics,
Shri Shivaji College ,Parbhani

1. Introduction

Gas sensors are the devices which are used to detect different types of toxic, hazardous, explosive and different types of gases. Increased environmental pollution, more motor vehicles, industrial wastes are the source of the toxic, explosive and inflammable gases in the environment of developed and developing countries. Some sensors from nature like ear, nose, skin, tongue, eyes; which are called as natural sensors. Other sensors that we had developed are known as artificial sensors. Now a days detection of gases presents in the atmosphere as well as gases produced in different natural and artificial phenomenon is of great importance. By detecting these gases like NO_2, NH_3, CO, CO_2, N_2, O_2, H_2S [1-4] etc. we can monitor the quality of air, we can analyse any particular reaction etc. Here comes the role of gas sensors. Gas sensors are the artificial sensors developed for detection of various gases and also their concentration. These gas sensors have application in variety of fields like security, automotive and industrial development, medical diagnostic and health products, weather station, detection of harmful gases etc.

Gas sensor is a device when it is exposed to gas its one or more physical / chemical properties changes. These changes in the properties can be measured directly and indirectly. Gas sensors are classified on the basis of gas sensing mechanism and change in different properties.

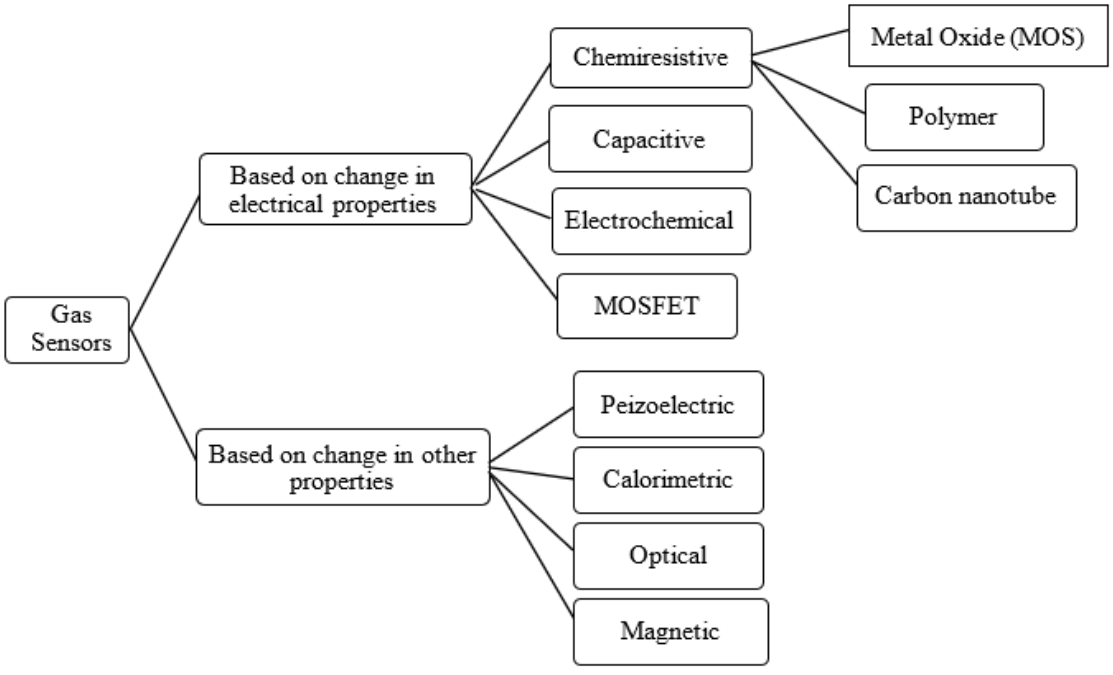

Fig. General Classification of sensors

Based on different electronic structures, Metal Oxide semiconductor gas sensors (MOS) are classified as :

1. Transition metal oxides (NiO, Fe_2O_3, Cr_2O_3 etc.)
2. Non transition metal oxides (Al_2O_3, MgO, SrO, SnO_2, ZnO etc.)

Development of these metal oxide semiconductor gas sensors, generally called as chemiresistive gas sensors [5], was started in 1957 by Bielanski et al. later in 1962 Seiyama developed ZnO film for sensing gases present in the environment. In 1972 taguchi developed sensing film by SnO_2[6] with greater stability. These efforts of developing sensing film for gas detection evolved in due course of time and created modern chemiresistive gas sensors. Chemiresistive gas sensor has following elements

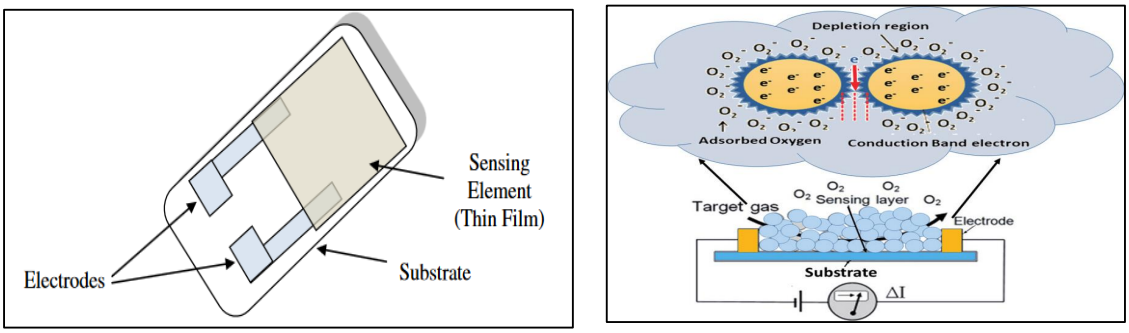

Fig. Typical Chemiresistive gas sensor sensing mechanism

Typical gas sensor consists of film of metal oxide (sensing element), substrate and electrodes for transducer action. When metal oxide film is heated, oxygen is adsorbed on the film by capturing free electrons. The depletion layer formed depends on size of semiconductor particles used. Conventionally in gas sensors, particle size is tens nano-meters. If particle size is small then sensitivity of sensor is high and vice versa. If the adsorbed oxygen concentration changes there is change in resistance which is recorded. All this information is converted into electrical signals with the help for transducer. Research community is continuously working towards to create good, reliable, highly sensitive film for gas sensing purpose. It has been observed that instead of pure metal if doped metal is used the sensitivity of gas sensor increases. In the present work the aryl diazonium salts are planned as dopant for improving the sensitivity and other characterization of MOS.

Diazonium salts or diazonium compounds are the group of organic compounds having functional formula $[R\text{-}N^{+}{\equiv}N]X^{-}$ where R can be any organic group such as alkyl or aryl and X is an inorganic or organic anion like halide. The stability of alkyl diazonium salt is very

low. But aryl diazonium salts are highly stable and hence find many applications in different field. Aryl diazonium salts increases the sensitivity of metal oxide gas sensors and are also biocompatible. Some of the examples of diazoniums compounds are benzene diazonium chloride, benzene diazonium hydrogen sulfate, 4-carboxybenzene diazonium salt, 4-Nitrobenzene diazonium salt etc.

2. Review of Literature and Development in the Subject:

Djamil Guettiche *et al* [7] a newly flexible nanocomposite-based nitrogen dioxide chemisensor was developed from poly- pyrrole filled with graphene functionalized by carboxybenzene diazonium salts using in situ one-step polymerization technique. Higher NO_2 selectivity was detected for this nanocomposite in comparison to several studied gases such as NO, NH_3,H_2S and CO_2. Moreover, its sensitivity remained considerable under varied temperature and humidity, indicating its good functionality and sta- bility under harsh environment, which might be offering it a longer working life. These researchers developed chemiresistive nitrogen oxide sensor based on nanocomposites developed with the help of carboxy benzene diazonium salts. Nanocomposites are within the size of 80 nm. It is used for NO_2 sensing. Here sensitivity increased (1.01% /ppm), faster response time (129 s), detention limit of (2 ppm) and reproducibility.

Asma Bensghaïer et al [8] designing new hybrid materials for sensing applications using Neural Red dye diazonium salt (DNR) was spontaneously reacted with MWCNTs in water at room temperature to synthesize CNT-NR nanohybrids. The CNT-NR hybrid was dispersed in dimethyl formamide (DMF) and drop casted on glass substrates for sensing of different volatile organic compounds (VOCs) and was observed to be highly selective towards acetone with response of 7.14% for 1000 ppm of acetone with response/recovery time of 47 and 49 s at room temperature (RT). Djamil

GUETTICHE *et al* [9] develop Nanocomposites of polypyrrole/reduced graphene oxide (PPy/rGO) and polypyrrole/ functionalized reduced graphene oxide with aryl 4-carboxybenzene diazonium salt (PPy/rGO-aryl-COOH) were prepared through covalent bonding by simple one-step chemical oxidative synthesis. The more enhanced NO_2 sensing properties have been shown by PPy/rGO- aryl-COOH in terms of higher sensitivity (1.01%/ppm), the faster response time (129 s), and the detection limit of (2ppm). Reproducibility features were also investigated.

Hamouma Ouezna *et al* [10] demonstrates that combining aryl diazonium-modified carbon nanotubes and in situ sonochemical polymerization on paper surface permits to

provide low cost, functional materials for gas sensors other paper electronic applications. Dipankar Saha *et al* [11] investigate modulating the chemical and mechanical surface properties of c-MoS_2 thin films using diazonium chemistry. In addition to a direct passivation strategy of c-MoS_2 with diazonium salts for electron-withdrawing groups, we also propose a novel *in situ* synthetic pathway for modification with electron-donating groups. In the present study Sonia Freddi *et al* [12,13] developed competitive and promising gas sensors for ammonia detection. Interestingly, present an easy and efficient method to functionalize graphene by using diazonium chemistry with different functional groups. Moreover, prove the superior sensing capability of our covalently modified graphene layers[14-18].

3. Objectives of Research/ Proposed Hypothesis:

Nowadays, there is increasing interest in highly sensitive, fast in response, accurate measurement smart gas sensors with excellent selectivity boosted by the high demand for environmental safety and healthcare applications. Significant research has been conducted to develop sensors based on novel highly sensitive and selective materials. Various efforts have been made to improve the sensing ability of chemiresistive-type sensors using various material with large number of dopants. A typical resistive type gas sensor shows a change in resistance upon exposure of gas molecules. An increase/decrease in resistance depends on the nature of the sensing material and target molecule. In view of these we use of aryl diazonium salt as dopant in metal oxides for optimizing smart material to gas sensor. Prepared thick film and measure different parameters of gas sensor like sensitivity, selectivity , low detection limit , response time, recovery time stability etc. These characteristics are studied in this research.

The research work comprises following main objectives :

1. To calcination, Sintering to a specific temperature different metal oxides for preparation of sensor.
2. To Prepare the Metal Oxides Composites with aryl diazonium salt for active material to fabricate Gas sensor.
3. To Prepare thin films using active material with different depositions Methods
4. To active material is investigated by characterization techniques like XRD, SEM, AFM, EDS etc.
5. To study the Sensing characteristics for different gases of prepared thin film sensors.
6. To optimize sensing material on the sensing parameters and investigation data of XRD,SEM,AFM and EDS.

4. Methodology to be adopted:

With the help of different deposition method, high quality films are prepared. Optimization of different parameters like temperature, thickness etc are done. Aryl diazonium salts are doped while preparing the Metal Oxides films. For optimize best material for sensing on the basis of electrical characterstics and characterisation techniques like X-ray diffraction (XRD), Scanning electron microscope (SEM), Atomic force microscope (AFM) etc are used. After characterisation, detailed analysis is done with respect to different parameters like sensitivity, selectivity , low detection limit , response time, recovery time stability etc.is done.

5. Importance Of Study / Society Application:

India is developing country and continuous growth is going on in different fields and industries. Due to different parameters, air pollution is increasing day by day. Nearly above 50% of pollutants comes from industrial waste and 30% from vehicles. These sectors releases harmful gases like CO, SO_2, NO_2, H_2S etc. There is very adverse effect of these harmful gases on the health of people and also there is degradation of quality of air. Due to this, global warming issues are increasing day by day. Peoples are facing severe health issues. Hence it is very important to detect these harmful gases present near to us so that we can take precautionary measures. Hence the development of cost effective, reliable, sensitive, fast gas sensor plays a significant role.

6. Proposed Plan of the work: Year-wise Plan of work and targets to be achieved:

Present work is planned for three years. Details of each year is listed below.

First Year:

a. In the first half of the year, mandatory course work is done along with the scrutiny of research paper related to proposed work.
b. Initiate synthesis of different undoped metal oxide materials.
c. The process of calcination, Sintering to a specific temperature different metal oxides for preparation of sensor
d. To Prepare the active composite material by metal oxides and aryl diazonium salt

Second Year:

a. To Prepare thin films using active material with different depositions Methods.
b. To characterize synthesized materials using XRD, SEM, AFM, EDS etc.
c. Initiate testing of Gas Sensor properties of aryl diazonium salt and Metal Oxide Composite thin films

Third Year:

a. To study the Sensing characteristics for different gases as-prepared thin film sensors.
b. To optimize sensing material on the sensing parameters.
c. Test of device properties of doped thin films.
d. Start publishing research papers.
e. Prepare thesis for submission.

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RESEARCH GUIDE **RESEARCH STUDENT**

Dr. Surendra M. Yenorkar **Mr. Sandip Anjiram Jadhav**
Professor,
Department of Physics and Electronics,
Shri Shivaji College, Parbhani,
Maharashtra-431401